Journal of Photochemistry & Photobiology, B: Biology 178 (2018) 395–403

Contents lists available at ScienceDirect

Journal of Photochemistry & Photobiology, B: Biology

journal homepage: www.elsevier.com/locate/jphotobiol

Photo-induced toxicity of tungsten oxide photochromic nanoparticles

A.L. Popov[a], N.M. Zholobak[b], O.I. Balko[b], O.B. Balko[b], A.B. Shcherbakov[b], N.R. Popova[a], O.S. Ivanova[c], A.E. Baranchikov[c], V.K. Ivanov[c,d,*]

[a] Institute of Theoretical and Experimental Biophysics, Russian Academy of Sciences, Pushchino, Moscow region 142290, Russia
[b] Zabolotny Institute of Microbiology and Virology, National Academy of Sciences of Ukraine, Kyiv D0368, Ukraine
[c] Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow 119991, Russia
[d] National Research Tomsk State University, Tomsk 634050, Russia

ARTICLE INFO

Keywords:
Tungsten oxide
Nanoparticles
Phototoxicity
Apoptosis
UV irradiation

ABSTRACT

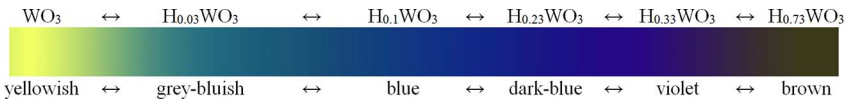
We synthesised a new type of photochromic tungsten oxide nanoparticles, analysed their photocatalytic activity and carried out a thorough analysis of their effect on prokaryotic and eukaryotic organisms. Ultrasmall hydrated tungsten oxide nanoparticles were prepared by means of hydrothermal treatment of tungstic acid in the presence of polyvinylpyrrolidone as a template, stabiliser and growth regulator. Tungstic acid was synthesised through an ion-exchange method using sodium tungstate solution and a strongly acidic cation exchange resin.

Upon illumination, photochromic nanoparticles of WO_3 were shown to increase greatly their toxicity against both bacterial (both gram-positive and gram-negative – *P. aeruginosa*, *E. coli* and *S. aureus*) and mammalian cells (primary mouse embryonic fibroblasts); under the same conditions, fungi (*C. albicans*) were less sensitive to the action of tungsten oxide nanoparticles. UV irradiation of primary mouse fibroblasts in the presence of WO_3 nanoparticles demonstrated a time- and dose-dependent toxic effect, the latter leading to a significant decrease in dehydrogenase activity and an increase in the number of dead cells. WO_3 nanoparticles were photocatalytically active under both UV light and even diffused daylight filtered through a window glass, leading to indigo carmine organic dye discolouration.

The obtained experimental data not only show good prospects for biomedical applications of tungsten trioxide, but also demonstrate the need for clear control of biosafety when it is used in various household materials and appliances.

1. Introduction

The modern technological paradigm requires research and development into new materials with specific physical and chemical properties. Recently, much attention has been paid to the development of various types of stimuli-responsive materials, which are able to change their characteristics in response to external factors. For instance, in the context of energy-saving, smart photo- or electrochromic materials have been developed which are able to control the throughput of visible light and solar radiation into buildings by having different transmittance levels depending on changing needs [1]. One of the most promising materials for photochromic films or coatings is nanocrystalline tungsten oxide, an n-type wide-bandgap semiconductor with a chemical type of chromism [2,3]. The electro-, photo- and chemochromic properties of tungsten oxide (WO_3) are widely used in electronic displays, optical modulators, windows with adjustable light transmission, rear-view mirrors in cars, etc. [4–7]. Under light irradiation, exposure to chemical reagents or the application of an electric field, stoichiometric WO_3 (faintly yellowish) undergoes a number of serial transformations, reversibly forming brightly coloured products [8]:



* Corresponding author.
E-mail address: van@igic.ras.ru (V.K. Ivanov).

https://doi.org/10.1016/j.jphotobiol.2017.11.021
Received 15 August 2017; Received in revised form 14 November 2017; Accepted 15 November 2017
Available online 20 November 2017

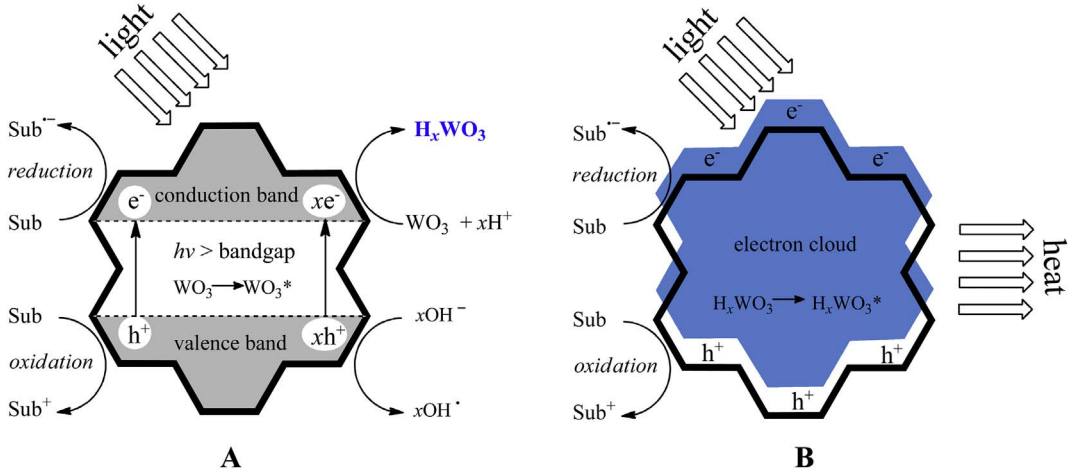


Fig. 1. Schematic diagram of the interaction mechanisms between light and WO_3 nanoparticles in semiconductor (A) and plasmonic (B) states. Photocatalysis, autophotoreduction and plasmonic heating are demonstrated.

In addition to the above-mentioned applications, tungsten oxide is one of the most thoroughly studied photocatalysts [9–15] for organic dye degradation. WO_3 nanoparticles of different morphologies, obtained by the hydrothermal-microwave method, have been shown to possess photocatalytic properties with respect to the discolouration of rhodamine B, indigo carmine and tetracycline hydrochloride under UV–vis irradiation [11]. WO_3 nanoparticles obtained by surfactant-assisted sonication have provided a high rate of rhodamine B and indigo carmine degradation under xenon lamp irradiation [12]. Multi-phase WO_3 samples possess improved photocatalytic activity, (as demonstrated by the bleaching of rhodamine B), that can be attributed to a decrease in the electron-hole recombination rate, owing to the formation of interphase junctions [13]. The efficient degradation of methylene blue dye by tungsten oxide nanoplates, synthesised using a hydrothermal or microwave-hydrothermal method, has been shown under UV light irradiation [14]. The photocatalytic activity of WO_3 nanoparticles (obtained by annealing $(NH_4)_xWO_{3-y}$ at 500 °C in air) and nanorods (prepared using a hydrothermal method using Na_2WO_4, HCl, $(COOH)_2$ and $NaHSO_4$ precursors at 200 °C) has been confirmed by the decomposition of methyl orange in an aqueous solution under UV light irradiation [15].

The common mechanism for organic dye degradation by photoactive semiconductor (photocatalyst) is represented in the left part of Fig. 1, A:

When a photocatalyst absorbs light that has an energy that exceeds the semiconductor's bandgap, an electron of the valence band is promoted to the conduction band, thus creating an electron (e^-)/hole (h^+) pair. Due to the semiconductor's photoexcitation ($WO_3 \rightarrow WO_3^*$) and the generation of electron/hole pairs, oxidation-reduction reactions take place at the surface: electrons reduce and holes oxidise the molecules of the surrounding substrate (Sub). Upon contact between the dye and the photoexcited nanoparticle, direct redox decomposition of the dye molecule occurs (Sub = Dye). More often, the first stage of photocatalysis is the redox transformation of water and/or oxygen (Sub = H_2O, O_2), forming the reactive oxygen species (ROS), which then destroy other substances, (the indirect redox decomposition of the dye molecule). Obviously, the photocatalytic activity of the material can affect not only the decomposition of organic dyes, but also the biological components of living cells.

The mechanism of tungsten oxide photo-induced chromism (autophotoreduction) is represented in the right part of Fig. 1, A. The excited electrons cause the reduction of tungsten (6 +) to (5 +) ions, leading to the formation of coloured, non-stoichiometric, hydrated tungsten oxide (H_xWO_3, $0 < x < 1$); the holes oxidise substrate (for example, water [16]), forming ROS, such as hydroxyl radicals. Upon contact with living cells, these ROS can cause oxidative stress, resulting in cell death. Another specific tungsten oxide feature is that it possesses photoactivity at a wide range of wavelengths. The most widely explored TiO_2-photocatalysts are effective under UV light only, while WO_3-based ones can change their bandgap upon irradiation, and thus tungsten trioxide could be an effective visible light photocatalyst, wherein the absorbed efficiency of sunlight can be enhanced enormously.

The autophotoreduction of tungsten oxide is accompanied by formation of free charge carriers, so photochromic colouration of tungsten oxide occurs due to the local surface plasmon resonance (LSPR) arising from appreciable free carrier concentrations [17,18]. It is well known that the interaction of plasmonic particles and light ($H_xWO_3 \rightarrow H_xWO_3^*$ photoexcitation) leads not only to redox processes on their surface (left part of Fig. 1, B), but also to the partial conversion of electromagnetic energy into heat (right part of Fig. 1, B). The volumetric generation of heat within the plasmonic nanoparticle $Q(\mathbf{r},t)$ is affected by the intensity of light, the particle's internal electromagnetic field distribution, and the thermal and electrical conductivity of the particle's material [18]:

$$Q(\boldsymbol{r},t) = \frac{1}{2}\sigma\tilde{\boldsymbol{E}}(\boldsymbol{r},t)\cdot\tilde{\boldsymbol{E}}^*(\mathbf{r},t);\ \sigma = \frac{4\pi nk}{\lambda_i \mu c}$$

where $\tilde{\boldsymbol{E}}(\boldsymbol{r},\boldsymbol{t})$ and $\tilde{\boldsymbol{E}}^*(\boldsymbol{r},\boldsymbol{t})$ are the generated electric field and its complex conjugate within the nanoparticles; σ – electrical conductivity at optical frequencies; λ_i – incident light wavelength; μ – relative magnetic permeability of the nanoparticle, and n and k – the real and imaginary parts of the refraction index of the nanoparticle, respectively. Plasmonic nanoparticles of non-stoichiometric tungsten oxide have been used for photothermal cancer treatment upon IR irradiation [18–23]. Thus, volumetric heating of WO_3 nanoparticles upon irradiation can bring an additional contribution to cytotoxicity, and thus should be taken into account.

For this paper, we synthesised a new type of photochromic tungsten oxide nanoparticles, analysed their photocatalytic activity and carried out a thorough analysis of their effect on prokaryotic and eukaryotic organisms. WO_3 nanoparticles possess both dark and light cytotoxicity, which significantly distinguishes them from common photocatalysts, and opens up new possibilities for their practical use.

2. Materials and Methods

2.1. Tungsten Oxide Nanoparticles

Ultrasmall tungsten oxide nanoparticles were synthesised by means of hydrothermal treatment of tungstic acid in the presence of